

AD-A285 412



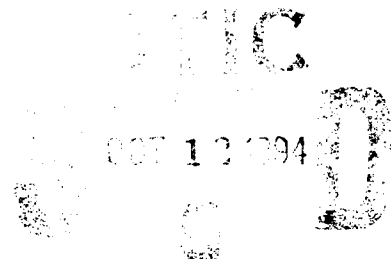
NAWCWPNS TP 8079

**Synthesis and Characterization of  
Tetranitraminocyclobutanes**

by

John W. Fischer  
Richard A. Hollins  
Charlotte K. Lowe-Ma  
Robin A. Nissan  
*Research Department*

SEPTEMBER 1994



**Naval Air Warfare Center Weapons Division  
China Lake, CA 93555-6001**



DTIC QUALITY INSPECTED 2

Approved for public release; distribution is unlimited.

94-32031



207

94

# **Naval Air Warfare Center Weapons Division**

## **FOREWORD**

A series of new nitramines have been synthesized. All of the new compounds possess four nitramine moieties arranged about a cyclobutane ring in a cis-trans-cis configuration. One of the new materials, CL-21, is exceptionally stable thermally and hydrolytically, yet very sensitive to impact. Because of this unique combination of properties, this new explosive may find applications as a pentaerythritol tetranitrate (PETN) replacement in a number of applications. Funding for this work was provided by the Naval Air Warfare Center Weapons Division (formerly Naval Weapons Center) Independent Research Funds and the Naval Sea Systems Command 6.2 Explosives Development Program.

This report has been reviewed for technical accuracy by William P. Norris and Andrew P. Chafin.

Approved by  
R. L. DERR, *Head*  
*Research Department*  
20 September 1994

Under authority of  
D. B. McKINNEY  
RAdm., U.S. Navy  
*Commander*

Released for publication by  
S. HAALAND  
*Deputy Commander for Research & Development*

NAWCWPNS Technical Publication 8079

Published by ..... Technical Information Department  
Collation ..... Cover, 9 leaves  
First printing ..... 110 copies

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE SEPTEMBER 1994	3. REPORT TYPE AND DATES COVERED Status FY86-90		
4. TITLE AND SUBTITLE  Synthesis and Characterization of Tetranitraminocyclobutanes		5. FUNDING NUMBERS Task R3103 Project R3103 Element 61152N		
6. AUTHORS John W. Fischer, Richard A. Hollins, Charlotte K. Lowe-Ma, and Robin A. Nissan				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Warfare Center Weapons Division China Lake, CA 93555-6001		8. PERFORMING ORGANIZATION REPORT NUMBER  NAWCWPNS TP 8079		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION /AVAILABILITY STATEMENT  A Statement; public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  (U) A series of new nitramines has been synthesized. All of the new compounds possess four nitramine moieties arranged about a cyclobutane ring in a cis-trans-cis configuration. One of the new materials, CL-21, is exceptionally stable thermally and hydrolytically, yet very sensitive to impact. Because of this unique combination of properties, this new explosive may find applications as a PETN replacement in a number of applications.				
14. SUBJECT TERMS  Cyclobutane, Explosives, and Nitramines			15. NUMBER OF PAGES 16	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT  UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE  UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT  UNCLASSIFIED	20. LIMITATION OF ABSTRACT  UL	

**UNCLASSIFIED**

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

## CONTENTS

Introduction .....	3
Discussion .....	3
Conclusions .....	11
Experimental Section .....	11
Preparation of Ureidoacetal 5 (Reference 2) .....	11
Preparation of 2-Imidazolidinone 6 (Reference 2) .....	11
Preparation of 1,3-Diacetyl-2-imidazolidinone 7 (Reference 2) .....	12
Preparation of Cyclobutyl Bis Acetylurea 8 (Reference 2) .....	12
Preparation of Cyclobutyl Bis Urea 9 (Reference 2) .....	12
Preparation of CL-21, 1 .....	12
Preparation of Primary Tetranitramine 3 .....	13
Preparation of Tetranitramine 2 .....	13
Preparation of Tetramethyl Tetraamine 10 .....	13
Preparation of Tetranitrosamine 13 .....	14
Preparation of Nitronitrosamine 14 .....	14
Preparation of Tetramethyl Tetranitramine 15 .....	14
References .....	15

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input checked="" type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail. or Special

## ACKNOWLEDGMENT

We thank Robert Chapman of Fluorochem. Corp., Azusa, Calif., for references and seminal suggestions leading to the synthesis of tetranitramine 2.

## INTRODUCTION

As part of our continuing effort to prepare new energetic materials with performance comparable to 1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) but with less hazard properties, we decided to investigate the synthesis of a series of cyclobutyl nitramines. Target compounds 1-3 were initially selected based on their calculated performance (Table 1) (Reference 1). These theoretical predictions, however, fail to take into account the strain energy of the cyclobutane ring (26 kilocalorie/mole (Kcal/mol)) suggesting that the actual performance of these compounds could exceed the predictions. The synthesis of these new nitramines are described below.

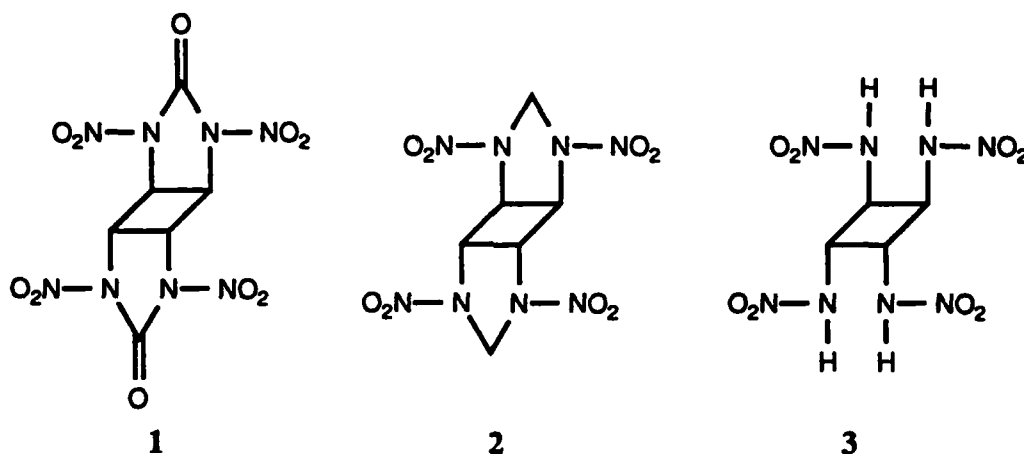


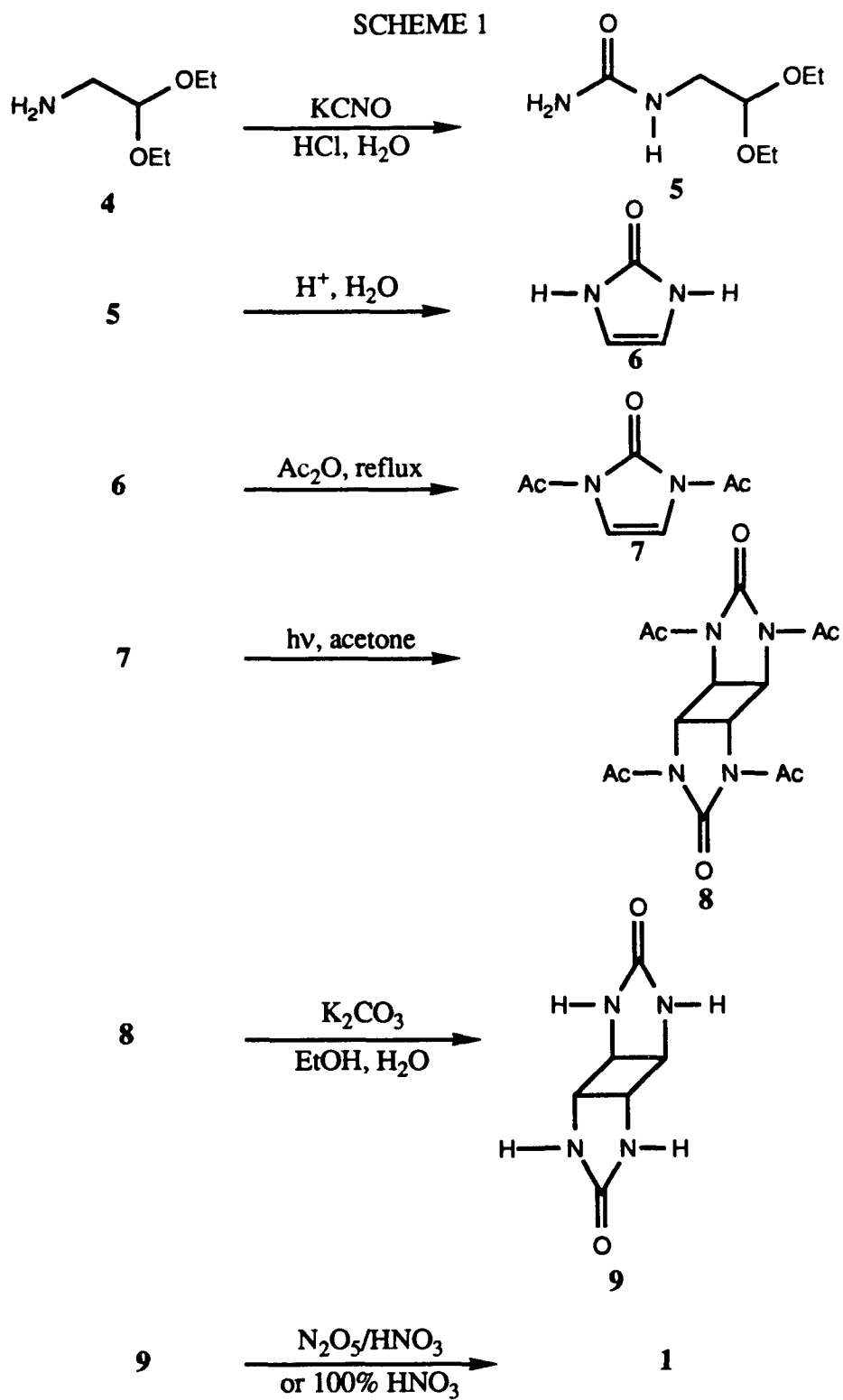
TABLE 1. Predicted Performance of Nitramines 1-3.

Properties	Compound 1	Compound 2	Compound 3
Density (g/cc)	1.99	1.85	1.83
Detonation pressure (Kbar)	328	321	388
Detonation velocity (mm/ $\mu$ s)	8.41	8.33	9.04

## DISCUSSION

The synthesis of nitramine 1 is outlined in Scheme 1 (Reference 2). Treatment of amino diethyl acetal, 4, treated with potassium cyanate in aqueous HCl yields urea acetal, 5, a white crystalline solid, which is dehydratively ring closed to imidazolidinone 6 in mild acid solution. Acetylation of 6 is easily accomplished in refluxing acetic anhydride to form

## SCHEME 1



diacetate 7. Irradiation of diacetate 7 dissolved in acetone with either a 200 or 550 watt medium pressure Hanovia lamp produces photo dimer 8 in approximately 20 to 30% yield. There is a competing polymerization during photolysis which presumably reduces the efficiency of this reaction. Further improvements in the efficiency of the photolysis may be possible by trying different solvents, photosensitizers, temperature, light source, wavelengths, etc. The desired dimer 8 precipitates from solution in a pure form and is collected by filtration. The photo dimerization produces exclusively the cis-trans-cis tetramine isomer as shown. Hydrolysis of the acetate groups is carried out in refluxing ethanol/water containing potassium carbonate forming bis urea 8. Nitration of 8 in either dinitrogen pentoxide/nitric acid solution or 100% nitric acid yields the desired nitramine 1. The final product must be washed thoroughly with water and dried. The concentration of the nitrogen pentoxide/nitric acid solutions used in the nitration step range from 7 to 25%. All nitration yields are high. If aqueous nitric acid is used, i.e., 70 or 90% nitric acid, there is some hydrolysis of the final product. Because nitramine 1 is under consideration as a potential replacement for pentaerythritol tetranitrate (PETN), we have designated this compound as CL-21. Some of CL-21's properties are shown in Table 2.

TABLE 2. Some Properties of CL-21.

Impact sensitivity (2.5 kg weight)	7.2 to 11 cm
Friction sensitivity, 795 lbs	10/10 no fire (NF)
Electrostatic sensitivity, 0.25 J	10/10 NF
TGA, <sup>a</sup> onset, °C	216
DSC, <sup>b</sup> exotherm, °C	240
Particle size, micrometer	22

<sup>a</sup> Thermogravimetric analysis.

<sup>b</sup> Differential scanning calorimetry

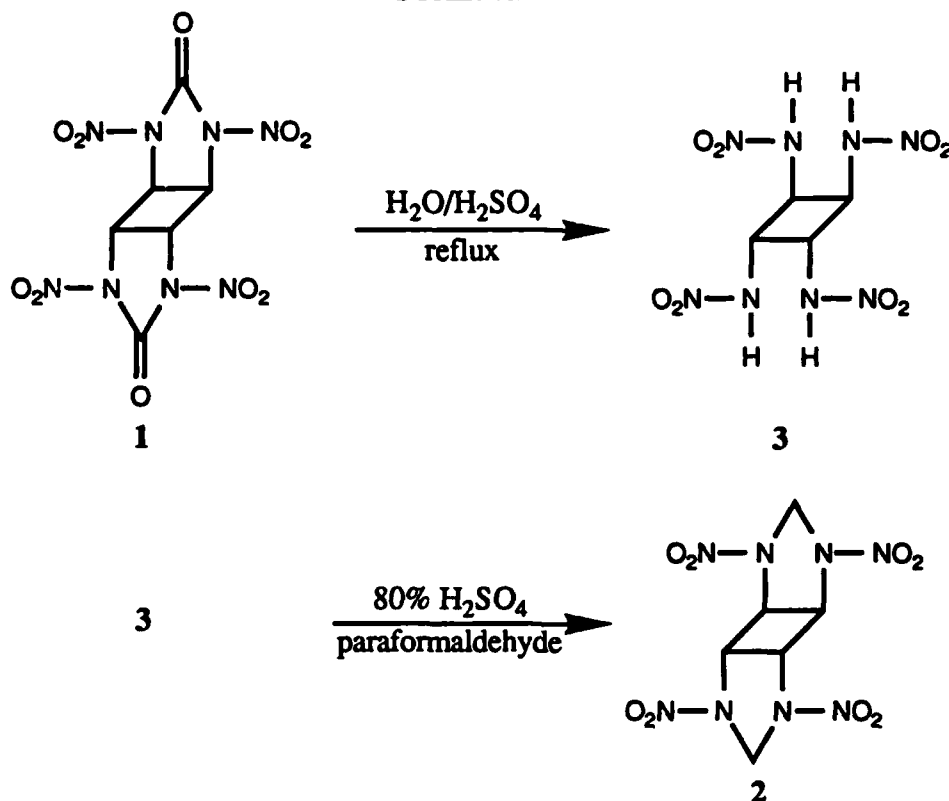
CL-21 is soluble in very polar organic solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO). When solutions of CL-21 in either DMF or DMSO are treated with water, the nitramine precipitates immediately as a fine white solid. Nitramine 1, a white solid, does not melt. At approximately 240°C, the material decomposes into a dark solid with evolution of a red gas. This material is surprisingly stable thermally, chemically, and hydrolytically when compared to similar materials such as dinitroglycoluril (DINGU) and tetranitroglycoluril (TINGU) (Reference 3). CL-21 can be heated at reflux for several hours in dilute sulfuric acid solutions before any decomposition is detected. Because of these unique properties, CL-21 is under consideration for scale-up and further investigation.

Nitramines 2 and 3 are derived from 1. The synthesis of these materials is outlined in Scheme 2.



Nitramine 1 is hydrolyzed to 3 in dilute sulfuric acid at reflux. After 6 to 8 hours, the white suspension slowly darkens in color and becomes a clear solution. Cooling, followed by concentration, causes 3 to precipitate out as a light brown solid. This primary nitramine is isomeric with HMX and should be handled with extreme caution. Although not measured, we predict this material to exhibit high impact and friction sensitivity and as such the amounts necessary for impact and friction measurements have not yet been made. Nitramine 3 does not melt. As the material is slowly heated, detonation occurs at approximately 156°C.

SCHEME 2



Treatment of 3 with paraformaldehyde in 80% aqueous H<sub>2</sub>SO<sub>4</sub> produces the methylene bridged nitramine 2 (Reference 4). The molecular structure of 2 was confirmed by an X-ray structure determination\* and is illustrated in Figure 1. The measured X-ray density of 2 is 1.82 grams/cubic centimeter (g/cc). The impact sensitivity of 2 is 19.1 centimeters (cm) (2.5 kilogram (kg) drop weight) and the differential scanning calorimetry (DSC) shows an exotherm at 248°C.

With bis urea 9 readily available, we further explored the synthesis of other cyclobutyl nitramines and nitrosamines. Alkylation and reduction of 9 is accomplished as shown in Scheme 3. Treatment of bis urea 9 with sodium hydride in tetrahydrofuran

\* Details of the X-ray structure determinations will be reported at a later date.

(THF) produces the expected tetrakis sodium salt. Alkylation of the salt followed by reduction with lithium aluminum hydride gives the amines 10-12. The alkylating agents employed are dimethyl sulfate, 10, ethyl iodide, 11, and isopropyl bromide, 12. The lithium aluminum hydride (LAH) reduction does not cleanly produce the expected amines (Reference 5) when R is ethyl or isopropyl (11 and 12). In these two cases, there is an appreciable amount of unreacted urea that cannot be removed from the desired product. Overall yields of 11 and 12 are low.

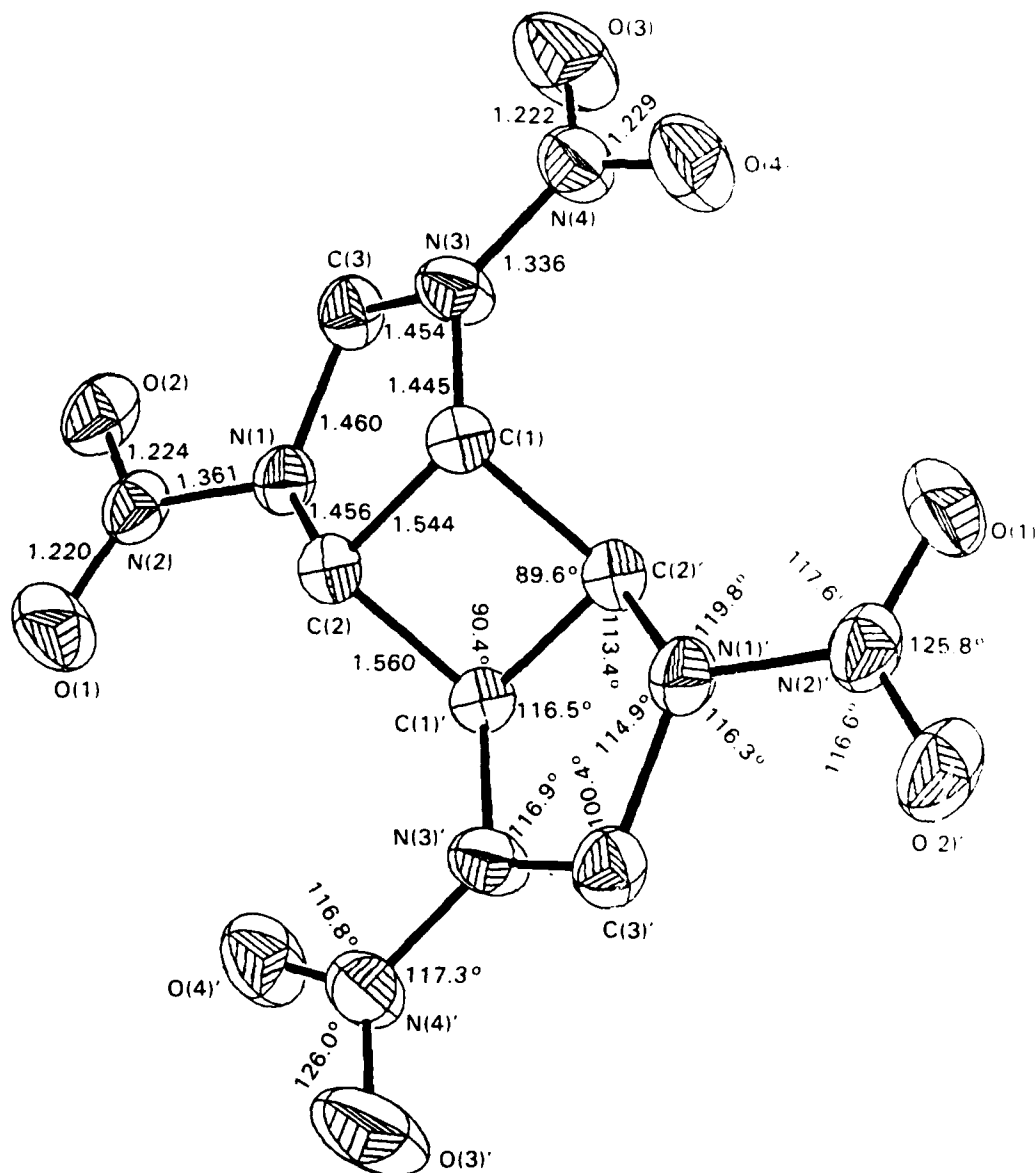
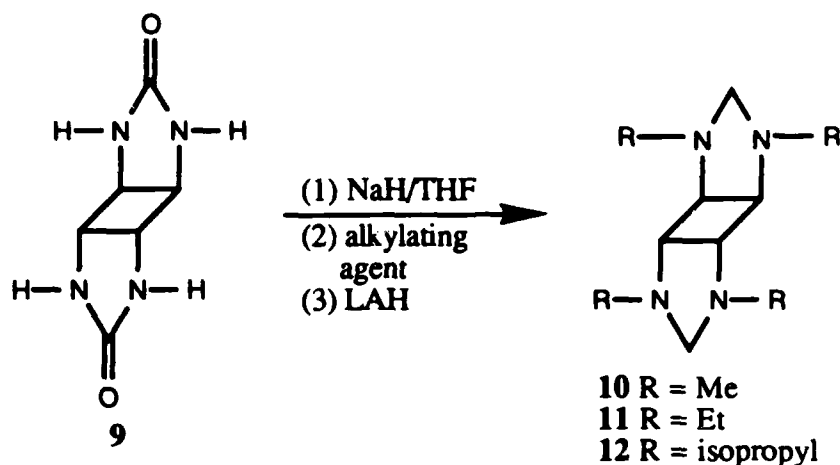


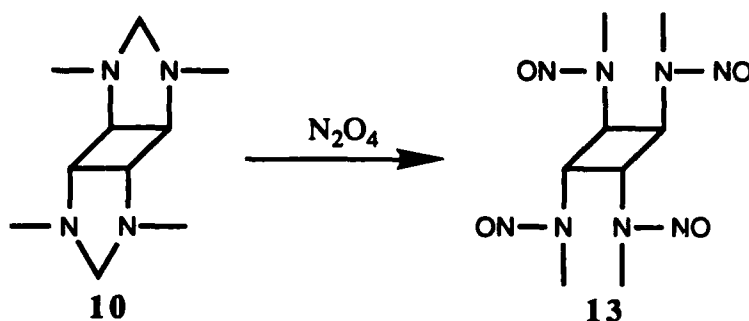
FIGURE 1. Plot of 2 Shown With 50% Probability Thermal Ellipsoids. Hydrogen atoms have been omitted for clarity.

## SCHEME 3



Tetramethyltetramine **10**, when treated with dinitrogen tetroxide, produces the tetranitrosamine **13** as shown in Scheme 4.

## SCHEME 4



The structure of **13** was confirmed by X-ray crystallography and is shown in Figure 2.\* Reaction of **11** and **12** with dinitrogen tetroxide are believed to give the corresponding tetranitrosamine as well. However, the yields of these transformations were very low and were not pursued further. Attempts to oxidize or nitrolyze **13** to the tetranitramine led to decomposition. No evidence of nitramine was detected.

When **10** is treated with dinitrogen pentoxide in chloroform, the mixed nitroso-nitramine **14** is formed (Scheme 5). The reaction mixture is complex and **14** is isolated after extensive purification. Other isomers are probably present, but not recovered. The structure of **14** has been confirmed by X-ray crystallography and is shown in Figure 3.\* A plausible mechanism for the formation of **14** has not yet been proposed. Since this compound is formed in low yield, it may be the product of the reaction between **10** and a

\* Details of the X-ray structure determinations will be reported at a later date.

combination of dinitrogen pentoxide and trace amounts of dinitrogen tetroxide which may be present from the thermal decomposition of  $N_2O_5$  (Reference 6).

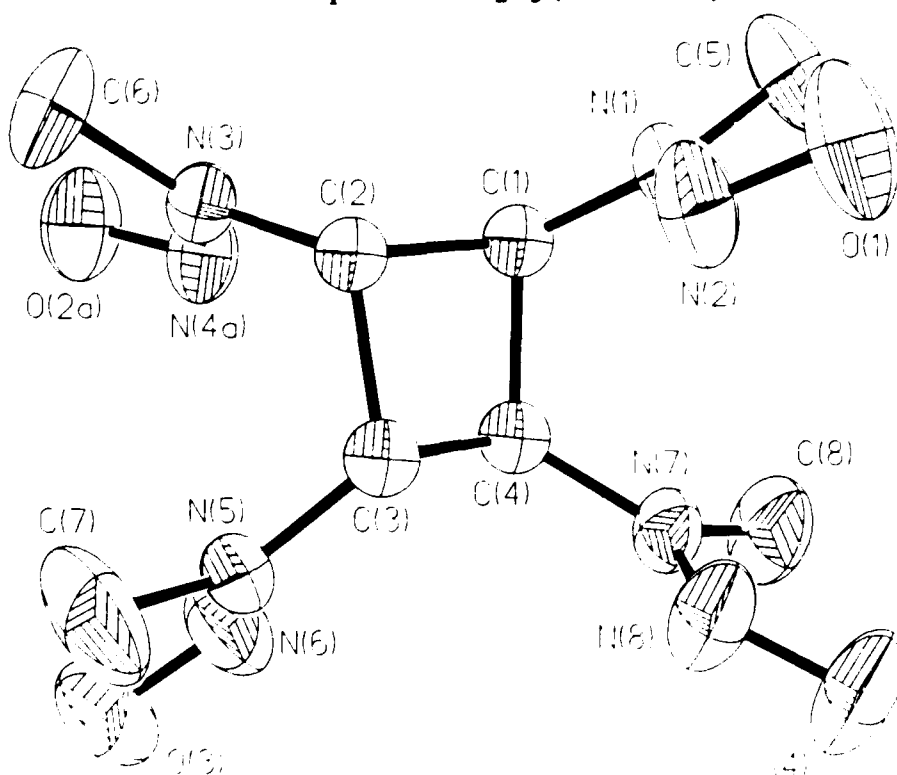
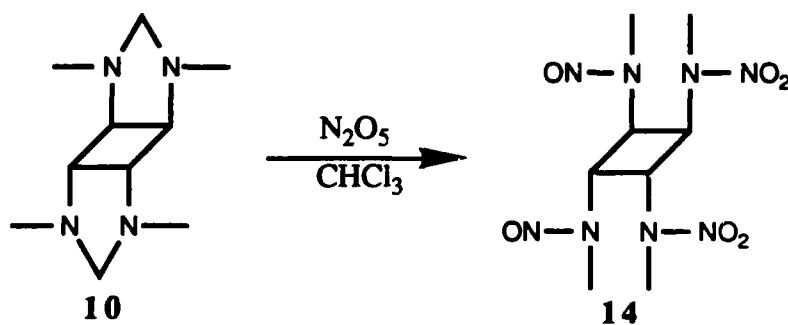


FIGURE 2. Plot of 13 is Shown With 50% Probability Thermal Ellipsoids. Hydrogen atoms have been omitted for clarity.

# SCHEME 5



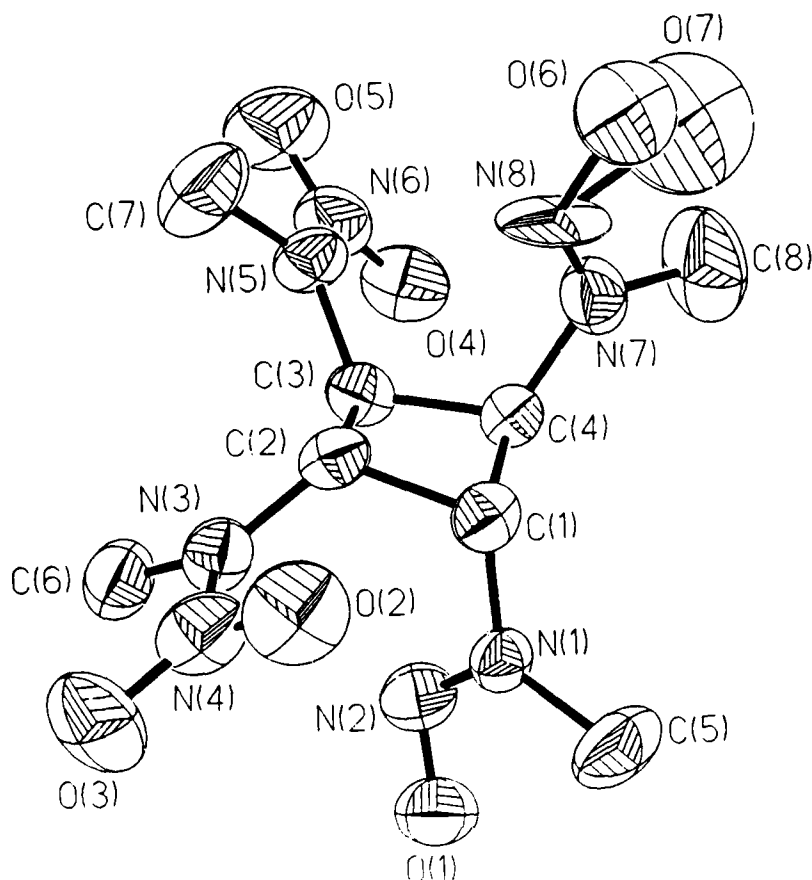
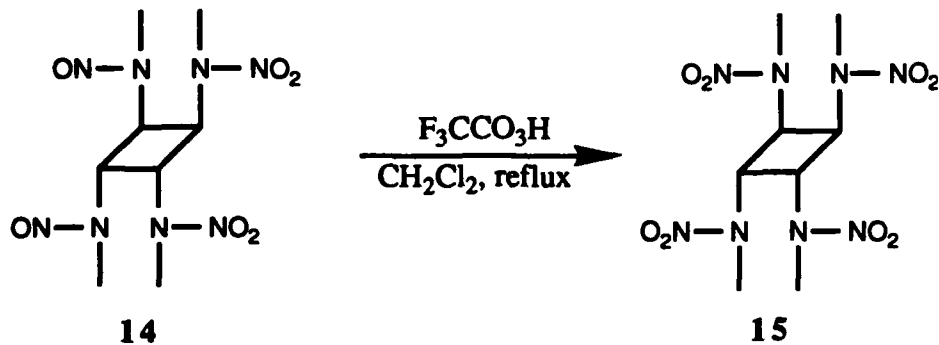


FIGURE 3. Plot of 14 is Shown With 50% Probability Thermal Ellipsoids. O(6) and O(7) are partially occupied positions representing disorder in that nitroso group. Hydrogen atoms have been omitted for clarity.

Nitrosodinitramine **14** is oxidized to the tetranitramine **15** using trifluoroperacetic acid in refluxing methylene chloride (Scheme 6). Nitramine **15** is thermally stable and somewhat energetic. No melting point is observed, but a detonation takes place at 256°C.

#### SCHEME 6



## CONCLUSIONS

A number of new energetic nitramines have been prepared. The common feature of each is a strained cyclobutane ring with the nitramine moieties arranged in a cis-trans-cis configuration. One of these compounds, CL-21, has been found to be particularly energetic and may find use as a PETN replacement in a number of applications.

## EXPERIMENTAL SECTION

Melting points were determined in capillary tubes with a Buchi 510 melting point apparatus. Infrared spectra were recorded with a Perkin-Elmer 137, 1330, or a Nicolet 7199 Fourier transform instrument. Proton and carbon magnetic resonance spectra were recorded on Nicolet NT-200 WB or IBM NR 80 instruments. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Mass spectra were recorded on a Hewlett-Packard Model 5985 instrument.

### PREPARATION OF UREIDOACETAL 5 (Reference 2)

Aminoacetaldehyde diethyl acetal 4 (38 milliliter (mL), 266 millimole (mmol)) was mixed with ice/water (55 gram (g)). To this slurry was added 5 N HCl (52.6 mL) pre-cooled to -40°C followed immediately by a solution of potassium cyanate (32 g, 400 mmol) in water (70 mL). The resulting solution was heated at reflux for 90 minutes, cooled to room temperature, and the volume concentrated to approximately one-third of the original amount. A white precipitate, 5, was collected by vacuum filtration and dried. The yield was 38 g (81%).

### PREPARATION OF 2-IMIDAZOLIDINONE 6 (Reference 2)

Ureidoacetal 5 (38 g, 216 mmol) was slurried with 0.1 N sulfuric acid (29.6 mL) and water (6.0 mL). The mixture was warmed to 55°C for an hour followed by addition of 1 N sulfuric acid (6.0 mL) with heating continued for an additional 2 hours. A strong smell of ethanol was evident; the clear colorless solution may develop a slight pink color. After cooling to ambient temperature, the clear solution was placed in a refrigerator overnight. The desired product, 6, precipitated from solution as white crystals (8.0 g, 44%).

**PREPARATION OF 1,3-DIACETYL-2-IMIDAZOLIDINONE 7 (Reference 2)**

2-Imidazolidinone 6 (10.7 g, 127 mmol) was refluxed in acetic anhydride for 2 hours. The solution was cooled to ambient temperature and the excess acetic anhydride and acetic acid were removed under reduced pressure, which gave approximately 18 g of 7 as an off-white solid. This represents a greater than 100% yield. Although this material is suitable for use directly in the next step, it can be purified by recrystallization from ethyl acetate giving 11.8 g of pure 7 (68% yield).

**PREPARATION OF CYCLOBUTYL BIS ACETYLUREA 8 (Reference 2)**

Diacetate 7 (100 g) was dissolved in acetone (4.5 liter (L)) and irradiated at room temperature with a 550 watt medium pressure Hanovia lamp in an immersion photolysis apparatus for a total of 8 days. The reaction was stopped at 4 days to collect the first batch of product 8, which precipitated from solution as a fine white solid. The filtered acetone solution was then irradiated for an additional 4 days. A total of 23.3 g of product was collected (23.3% yield). Yields can range up to 30%. This photolysis also works using a 200 watt lamp although with slightly decreased yields. There is a competing polymerization reaction that keeps the yield of the desired dimerization reaction low.

**PREPARATION OF CYCLOBUTYL BIS UREA 9 (Reference 2)**

Photodimer 8 (450 milligram (mg), 1.3 mmol) was suspended in a solution of 95% ethanol (15 mL) and water (5 mL) containing potassium carbonate (370 mg, 2.7 mmol) and heated at reflux for 4 hours. The fine white solid, bis urea 9, which precipitated from solution was filtered and dried. The yield was 188 mg (86%) of 9. This reaction can be easily scaled up to much larger sizes.

**PREPARATION OF CL-21, 1**

Bis urea 9 (250 mg, 1.5 mmol) was added in portions to a stirred solution of 25% dinitrogen pentoxide in nitric acid at 0°C. The resulting white suspension was slowly allowed to warm to ambient temperature and stirred overnight. Vacuum filtration of the white suspension, with thorough washing with water and drying, gave desired nitramine 1 in 97% yield (0.50 g). This reaction works equally as well with lower concentration dinitrogen pentoxide solutions or even neat 100% nitric acid. High yields are still achieved when scaled up to 2-3 g of bis urea 9.

<sup>1</sup>H NMR (DMSO d-6): δ 5.51 s. <sup>13</sup>C NMR (DMSO d-6): δ 141.2, 55.0. IR (KBr, cm<sup>-1</sup>): 3030, 3000, 1810, 1580, 1310, 1250, 1100. Elemental analysis: calculated for C<sub>6</sub>H<sub>4</sub>N<sub>8</sub>O<sub>10</sub>: % C, 20.70; % H, 1.16; % N, 32.19. Found: % C, 20.40; % H, 1.20; % N, 32.39.

**PREPARATION OF PRIMARY TETRANITRAMINE 3**

Nitramine 1 (2.8 g, 8 mmol) was suspended in water (50 mL) containing sulfuric acid (1 mL) and refluxed with vigorous stirring until the solid completely dissolves, approximately 4-6 hours. The resulting light brown solution is cooled and concentrated until a brown precipitate forms. The primary tetranitramine 3 was collected by vacuum filtration as a beige amorphous solid (0.87 g, 36% yield).

$^1\text{H}$  NMR (DMSO  $d_6$ ):  $\delta$  10.76 s, 4 H; 4.80 s, 4 H.  $^{13}\text{C}$  NMR (DMSO  $d_6$ ):  $\delta$  52.9. IR (KBr,  $\text{cm}^{-1}$ ): 3280, 3000, 1585, 1400, 1350.

**PREPARATION OF TETRANITRAMINE 2**

Nitramine 3 (500 mg, 1.7 mmol) was added to a stirring solution of paraformaldehyde (120 mg, 4.0 mmol) in 80% sulfuric acid (5 mL) at  $-5^\circ\text{C}$ . The brown suspension was stirred for 45 minutes then poured into ice water (20 mL) and the light brown solid, nitramine 2 (174 mg, 32%), was collected and dried by vacuum filtration. Crystal suitable for an X-ray structure determination was grown from 100% nitric acid.

$^1\text{H}$  NMR (DMSO  $d_6$ ):  $\delta$  5.44 s, 4 H; 5.82 s (slightly broadened), 4 H.  $^{13}\text{C}$  NMR (DMSO  $d_6$ ):  $\delta$  67.8 t, 62.4 d. IR (KBr,  $\text{cm}^{-1}$ ): 2970, 1520, 1390, 1295, 755, 575. Mass Spec (chemical ionization, methane):  $M^+ + 1 = 321$ ; mp =  $228^\circ\text{C}$  (dec)

**PREPARATION OF TETRAMETHYL TETRAAMINE 10**

Bis urea 9 (0.75 g, 4.5 mmol) was added in one portion to sodium hydride (0.52 g, 21 mmol) suspended in THF at ambient temperature. This mixture was stirred for 45 minutes followed by addition of dimethyl sulfate (2.03 mL, 21 mmol) and then heated at reflux overnight. After cooling to room temperature, the cloudy white solution was filtered and solvent removed under reduced pressure to yield the crude tetramethyl bis urea (0.92 g) as a white solid. Purification was accomplished by recrystallization from hot acetone to give the desired intermediate (0.43 g, 50% yield) as a white solid.

$^1\text{H}$  NMR (DMSO  $d_6$ ):  $\delta$  3.91 s, 4 H; 2.71 s, 12 H.  $^{13}\text{C}$  NMR (DMSO  $d_6$ ):  $\delta$  159.7, 58.2, 28.1. IR (KBr,  $\text{cm}^{-1}$ ): 2900, 1650, 1440, 1390, 1200, 920; mp =  $242-250^\circ\text{C}$  (dec).

Lithium aluminum hydride (1.4 g, 37 mmol) was added to the above tetramethyl bis urea (436 mg, 1.9 mmol) suspended in THF at ambient temperature followed by stirring for 3 days under nitrogen. The resulting suspension was carefully quenched by adding water (10 drops), 1 M NaOH (10 drops), and water (10 drops), drying ( $\text{MgSO}_4$ ) and removing solvent under reduced pressure to give an oil/solid. Sublimation of the crude product at 0.1 torr gave the desired tetramethyl tetramine 10 (275 mg) in 72% yield.



$^1\text{H}$  NMR (DMSO  $d_6$ ):  $\delta$  3.38 AB quartet q,  $J = 6.3$  Hz, 4 H; 3.27 s, 4 H; 2.29 s, 12 H.  $^{13}\text{C}$  NMR (acetone  $d_6$ ): 78.6, 64.6, 38.4. IR (KBr,  $\text{cm}^{-1}$ ): 2920, 1460, 1440, 1360, 1215, 1145, 1095, 995; mp = sublimes at  $55^\circ\text{C}$  at 0.1 torr.

### PREPARATION OF TETRANITROSAMINE 13

Dinitrogen tetroxide (5 mL) was added in one portion to tetramine 10 (100 mg, 0.5 mmol) in carbon tetrachloride (5 mL) at room temperature. The deep red solution was stirred overnight and then carefully poured into water (25 mL). This two phase mixture was extracted with methylene chloride (3 x 20 mL). The organic extracts were combined, washed with saturated sodium bicarbonate (20 mL), brine (20 mL), dried ( $\text{MgSO}_4$ ), and solvent removed under reduced pressure giving tetranitrosamine 13 (100 mg, 68%) as a yellow solid.

$^1\text{H}$  NMR (DMSO  $d_6$ ):  $\delta$  3.00 s, 12 H; 6.19 s, 4 H.  $^{13}\text{C}$  NMR (DMSO  $d_6$ ):  $\delta$  61.4 d, 33.2 q. IR (KBr,  $\text{cm}^{-1}$ ): 3020, 1435, 1345, 1210, 1125, 1045; mp =  $247\text{--}249^\circ\text{C}$  (dec).

### PREPARATION OF NITRONITROSAMINE 14

Dinitrogen pentoxide in chloroform (0.8 M, 5 mL) is added directly to tetramethyl tetramine 10 (56 mg, 0.3 mmol) at  $0^\circ\text{C}$  followed by stirring for 2.5 hours. The reaction was quenched with saturated sodium bicarbonate (25 mL), and extracted with chloroform (25 mL). Washing the organic layer with brine (25 mL), drying ( $\text{MgSO}_4$ ), and removal of solvent afforded a white solid (34 mg). Purification on silica gel eluting with 75% ethyl acetate in hexane followed by recrystallization from ethyl acetate gave the nitronitrosamine 14 as a white crystalline solid (yield approximately 2 mg, 2%).

$^1\text{H}$  NMR (acetone  $d_6$ ):  $\delta$  5.7 m, 4 H; 3.44 m, 6 H; 3.10 m, 6 H. IR (KBr,  $\text{cm}^{-1}$ ): 3010, 2940, 1520, 1435, 1355, 1300, 1250. Mass Spec (chemical ionization, methane):  $\text{M}^+ + 1 = 321$ ; mp =  $207\text{--}209^\circ\text{C}$  (dec).

### PREPARATION OF TETRAMETHYL TETRANITRAMINE 15

Nitrosanitramine 14 (78 mg, 0.24 mmol) was added to a solution of trifluoro peracetic acid (made *in situ* by addition of 1.5 mL of 90% hydrogen peroxide to 9.6 mL of trifluoroacetic anhydride in 15 mL of methylene chloride) in methylene chloride at  $0^\circ\text{C}$ . After 5 minutes, the solution was refluxed for 4 hours. The reaction is then cooled, quenched with saturated sodium bicarbonate and extracted with chloroform (2 x 25 mL). Combining the organic layers, washing with water (25 mL), brine (25 mL), drying ( $\text{MgSO}_4$ ), and removal of solvent afforded the desired tetranitramine 15 (40 mg, 47% yield) as a white solid.

$^1\text{H}$  NMR (acetone  $d_6$ ):  $\delta$  5.78 s, 4 H; 3.47 s, 12 H.  $^{13}\text{C}$  NMR (DMSO  $d_6$ ):  $\delta$  88.4, 59.5. IR (KBr,  $\text{cm}^{-1}$ ): 2920, 1510, 1420, 1360, 1285; mp =  $262^\circ\text{C}$  (det).

## REFERENCES

1. (a) L. R. Rothstein and R. Petersen. "Predicting High Explosive Detonation Velocities from their Composition and Structure," *Prop. and Explo.*, Vol. 4 (1979), pp. 56-60; (b) L. R. Rothstein. "Predicting High Explosive Detonation Velocities from their Composition and Structure," *Prop. and Explo.*, Vol. 6 (1981), pp. 91-3; (c) Naval Surface Weapons Center. *Estimation of Normal Densities of Explosive Compounds From Empirical Atomic Volumes*, by D. A. Cichra, J. R. Holden, and C. Dickinson, Silver Spring, Md., NSWC, February 1980. 39 pp. (TR79-273, publication UNCLASSIFIED.)
2. (a) G. Steffan and G. O. Schenck. "Lichtreaktionen der 1,3-Diacetyl-D<sup>4</sup>-imidazolinone-(2)," *Chem. Ber.*, 100 (1967), 3961; (b) R. Duschinsky and L. A. Dolan. "Studies in the Imidazolone Series. The Synthesis of a Lower and a Higher Homolog of Desthiobiotin and of Related Substances" *J. Am. Chem. Soc.*, 68 (1945), 2350; (c) H. D. Scharf and W. Thunker. "Darstellung von r-1, c-2, t-3 t-4-Cyclobutantetraamin," *Liebigs Ann. Chem.*, 1979, 605; (d) R. A. Whitney. "Cycloaddition Reactions of 1,3-Diacetylimidazolin-2-one," *Tetrahedron Lett.*, 22 (1981), 2063.
3. (a) Y. Oyumi and T. B. Brill. "Thermal Decomposition of Energetic Materials XXVIII. Predictions and Results for Nitramines of Bis-imidazolininedione: DINGU, TNGU, and TDCD," *Prop., Explo., Pyrotech.*, 13 (1988), 69; (b) R. Meyer. *Explosives*, 3rd ed., New York, VCH, 1987. p. 103.
4. (a) L. Goodman. "Condensations of Primary Aliphatic Nitramines with Formaldehyde," *J. Am. Chem. Soc.*, 75 (1953), 3019; (b) W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton, and C. E. Maxwell, III. "The Nitration of Derivatives of Ethylenediamine," *J. Am. Chem. Soc.*, 72 (1950), 3132.
5. H. A. Bates, N. Condulis, and N. L. Stein. "Reduction of Cyclic Ureas with Lithium Aluminum Hydride," *J. Org. Chem.*, 51 (1986), 2228.
6. J. W. Fischer. *The Chemistry of Dinitrogen Pentoxide. Nitro Compounds: Recent Advances in Synthesis and Chemistry*, H. Feuer and A. T. Nielsen, eds., New York, VCH, 1990. p. 267.

**INITIAL DISTRIBUTION**

- 1 Naval Air Systems Command, Arlington (AIR-540T, Thomas)
- 2 Chief of Naval Research, Arlington
  - OCNR-253, D. Siegel (1)
  - OCNR-332PE, Dr. R. S. Miller (1)
- 5 Naval Sea Systems Command, Arlington
  - SEA-62D, C. M. Christensen (1)
  - SEA-661 (1)
  - SEA-665 (2)
  - SEA-96R, Dr. J. Pastine (1)
- 1 Commander in Chief, U. S. Pacific Fleet, Pearl Harbor (Code 325)
- 1 Commander, Third Fleet
- 1 Commander, Seventh Fleet
- 1 Marine Corps Combat Development Command, Marine Corps Air-Ground Task Force Warfighting Center, Quantico (WFO6B, Scientific Advisor)
- 1 Naval Explosive Ordnance Disposal Technology Center, Indian Head (Code D, L. Dickinson)
- 3 Naval Research Laboratory
  - Code 2627 (1)
  - Code 6030, Dr. R. Gilardi (1)
  - Code 6120, Dr. A. Garroway (1)
- 1 Naval Surface Warfare Center, Crane Division, Crane (Code 5063, Dr. H. Webster III)
- 9 Naval Surface Warfare Center, Dahlgren Division, White Oak Detachment, Silver Spring
  - Code R10C, S. Collignan (1)
  - Code R101, L. Roslund (1)
  - Code R11
    - Dr. M. Sitzmann (1)
    - C. Gotzmer (1)
    - Dr. W. Koppes (1)
    - K. F. Mueller (1)
    - J. M. Short (1)
    - Dr. A. Stern (1)
  - Code R13, Dr. R. Doherty (1)
- 3 Naval Surface Warfare Center Indian Head Division, Indian Head
  - Code 5253, W. G. Roger (1)
  - Code 5253L, J. Moniz (1)
  - Code R16, J. Consaga (1)
- 1 Naval War College, Newport (Technical Library)
- 1 Naval Weapons Station, Yorktown (Assistant Director, Naval Explosives Development Engineering Department)
- 1 Office of Naval Technology, Arlington (ONT-21, Dr. E. Zimet)
- 1 Army Missile Command, Redstone Arsenal (L. Aseoka)
- 4 Army Ballistic Research Laboratory, Aberdeen Proving Ground
  - DRXBR-IBD
    - Director (1)
    - A. Junasz (1)
    - Dr. I. W. May (1)
  - AMXBR-TBD, J. J. Rocchio (1)
- 1 Army Research Office, Research Triangle Park (R. Ghirardelli)
- 1 Ballistic Missile Defense Advanced Technology Center, Huntsville (D. C. Sayles)
- 1 Air Force Wright Laboratory, Armament Directorate, Eglin Air Force Base (WL/MNF, O. K. Heiney)
- 1 Headquarters, 497 IG/INT, Falls Church (OUWG Chairman)

- 2 Phillips Laboratory, Edwards Air Force Base
  - OL AC PL/RKCP, L. Dee (1)
  - Technical Library (1)
- 1 Advanced Research Projects Agency, Arlington (Dr. R. Loda)
- 2 Defense Technical Information Center, Alexandria
- 4 Lawrence Livermore National Laboratory, Livermore, CA
  - Dr. R. L. Atkins (1)
  - Dr. A. R. Mitchell (1)
  - Dr. P. F. Pagoria (1)
  - Dr. R. L. Simpson (1)
- 1 Los Alamos National Laboratory, Los Alamos, NM (Dr. M. A. Hiskey)
- 3 Aerojet General Facility, Sacramento, CA
  - Department 5400 (1)
  - Dr. T. C. Archibald (1)
  - T. C. Manser (1)
- 1 Analy-Syn Laboratories, Incorporated, Paoli, PA (Dr. V. Keenan)
- 5 Atlantic Research Corporation, Gainesville, VA
  - G. T. Bowman (1)
  - K. Graham (1)
  - R. E. Shenton (1)
  - W. Waesche (1)
  - B. Wheatley (1)
- 1 Center for Naval Analyses, Alexandria, VA (Technical Library)
- 1 Fluorochem, Incorporated, Azusa, CA (Dr. K. Baum)
- 1 Hercules, Incorporated, Allegany Ballistics Laboratory, Rocket Center, WV
  - (Dr. K. D. Hartman)
- 1 Hercules, Incorporated, Magna, UT (G. Butcher)
- 2 Rockwell International Corporation, Rocketdyne Division, Canoga Park, CA
  - Dr. K. Christe (1)
  - Dr. J. Weber (1)
- 2 SRI International, Menlo Park, CA
  - Dr. Bottaro (1)
  - Dr. R. Schmitt (1)
- 1 Teledyne, McCormick Selph, Hollister, CA (Dr. N. Ogimachi)
- 2 The Ensign-Bickford Company, Simsbury, CT
  - C. N. Kaiser (1)
  - Dr. P. F. Meunier (1)
- 1 The Johns Hopkins University, Chemical Propulsion Information Agency, Columbia, MD
  - (T. Christian)
- 1 Thiokol Corporation/Elkton Division, Elkton, MD (E. Sutton)
- 1 Thiokol Corporation/Huntsville Division, Huntsville, AL (Dr. W. Graham)
- 1 Thiokol Corporation/Longhorn Division, Marshall, TX (Dr. D. Dillahay)
- 2 Thiokol Corporation/Shreveport Division, Shreveport, LA
  - L. Estabrook (1)
  - Dr. J. West (1)
- 3 Thiokol Corporation, Utah Division, Brigham City, UT
  - D. A. Flanigan (1)
  - G. Thompson (1)
  - R. Wardle (1)
- 1 3M Corporation, St. Paul, MN (T. Manzara, Bldg. 236GB)
- 1 Unidynamics/Phoenix, Incorporated, Phoenix, AZ (Dr. T. W. Fronabarger)
- 1 United Technologies Corporation, San Jose, CA (CSD Library)